



## DIAMOND-LIKE ORDER IN ZINC-BLENDE COMPOUNDS

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We show that the energy of substitutional randomization of atoms in zinc-blende compounds is surprisingly small. This suggests the existence of a new class of defects in these materials ("random aggregates"), which consist of regions of  $\lesssim 10$  atoms where the sites of the diamond lattice are randomly occupied by A or B atoms in place of the ordered AB crystal occupancy. The structural and electronic properties of these defects are outlined.

Substitutionally disordered phases appear above a critical temperature in many semiconductor alloys<sup>1</sup> and ternary compounds,<sup>2,3</sup> such as  $\text{Ge}_x\text{Si}_{1-x}$ ,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , and  $\text{CuInSe}_2$ . In this paper, we investigate the possibility of substitutional disorder (not amorphization) in zinc-blende III-V and II-VI semiconductors. We find that the enthalpy needed to transform these materials from the ordered zinc-blende structure, in which cations and anions occupy different sublattices, to a random diamond-like structure, in which each sublattice is equally occupied by cations or anions, is surprisingly small, compared with antisite formation energies. Although the disordered diamond-like phase is not thermodynamically stable as a macroscopic crystal, small regions (e.g.,  $\lesssim 10$  atoms) of such substitutional disorder can exist below the melting point of the crystal. Such regions form a new class of crystal defects, which we call "random aggregates" (RAs), with formation energies *per cluster* comparable to those of *single* point defects. We will outline the expected structural and electronic properties of these defects.

The randomization energy,  $\Delta E_R = E(\text{random}) - E(\text{ordered})$ , of an ordered compound has two major components:<sup>4,5</sup> size mismatch and valence mismatch. Size mismatch dominates in isovalent systems, including IV-IV alloys ( $\text{Ge}_x\text{Si}_{1-x}$ ), which form a diamond-like disordered phase, and pseudobinary III-V alloys ( $\text{GaAs}_{1-x}\text{Sb}_x$ ,  $\text{Ga}_x\text{In}_{1-x}\text{P}$ ), which, upon randomization of the isovalent atoms, form a zinc-blende-like disordered phase. The energy difference reflects the fact that certain or-

dered structures better accommodate the strain resulting from atomic size mismatch than does the random alloy. For the chalcopyrite structure of  $\text{GaAs}_{0.5}\text{Sb}_{0.5}$ ,<sup>4</sup>  $\Delta E_R = 8.5$  meV/atom at  $T=800$  K. In non-isovalent  $\text{ABC}_2$  compounds (e.g.,  $\text{CuInSe}_2$ ) an additional contribution to the enthalpy of randomization comes from the valence mismatch.<sup>2,3,5</sup> These occur when some of the  $\text{C-A}_2\text{B}_2$  tetrahedra of the ordered chalcopyrite structure, which satisfy the octet rule, are replaced in the disordered phase by  $\text{C-A}_3\text{B}$  and  $\text{C-AB}_3$  tetrahedra, which do not satisfy the octet rule individually. The enthalpy of cation randomization in  $\text{CuInSe}_2$  is 20 meV/atom.<sup>3</sup>

In this context, it is interesting to examine the enthalpy of randomization for common zinc-blende (ZB) semiconductors, such as GaAs. In the ordered ZB structure, each of the two fcc sublattices is occupied exclusively by either Ga or As. On the other hand, the hypothetical perfectly random structure contains equal numbers of Ga and As atoms on each sublattice, and exhibits a diamond-like diffraction pattern. Each lattice site is surrounded by one of five possible tetrahedra:  $\text{Ga}_4$ ,  $\text{Ga}_3\text{As}_1$ ,  $\text{Ga}_2\text{As}_2$ ,  $\text{Ga}_1\text{As}_3$ ,  $\text{As}_4$ . (In the ZB structure, a Ga atom is always surrounded by four As atoms and an As atom by four Ga atoms.) The enthalpy of randomization in this non-isovalent system is dominated by the cost of forming "wrong" Ga-Ga and As-As bonds that do not individually satisfy the octet rule. Since half of the atoms in the random structure will be on the correct sites and half on anti-sites, one might have guessed that the enthalpy of randomization can be approximated by  $\bar{E}/2$  per atom, where  $\bar{E}$  is the average energy for the formation of the two types of antisites from the perfect crystal. For example, let us look at GaAs and ZnSe, which have been investigated with first-

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principles pseudopotential calculations by Baraff and Schlüter<sup>6</sup> for GaAs, and Laks *et al.*<sup>7</sup> for ZnSe. The average formation energy relative to the perfect crystal,  $\Delta E_N = 2\bar{E}$ , for neutral (N) isolated antisite defect pairs is 6.2 eV in GaAs and 9.5 eV in ZnSe, or 0.78 eV and 1.19 eV per wrong bond (WB), respectively. The estimated randomization energy would then be  $\bar{E}/2 = 1.55$  eV for GaAs and 2.38 eV for ZnSe. As a model for the alloy, however,  $\bar{E}/2$  is a substantial overestimate because it overlooks the effects of charge compensation and defect condensation. First, transferring two electrons from the donor-like  $\text{As}_{\text{Ga}}$  to the acceptor-like  $\text{Ga}_{\text{As}}$  in GaAs reduces the energy of the pair to 4.5 eV.<sup>6</sup> This charge transfer gain,  $\Delta E_{CT} = -1.7$  eV per pair, equals twice the donor-acceptor band gap of 1.2 eV (the difference between the donor and the acceptor levels) minus the electron-electron repulsion,  $U = 0.7$  eV. Second, placing the two antisite defects on neighboring sites allows a further energy reduction because the number of wrong bonds is reduced from eight to six, and because of the gain in Coulomb attraction between the two charged defects. This condensation energy gain,  $-\Delta E_C$ , reduces the total energy to 1.8 eV per defect pair, or 0.3 eV/WB.<sup>6</sup> In ZnSe the two types of antisite defects introduce closely spaced (mid-gap) levels, so the donor-acceptor band gap is nearly zero; consequently,  $\Delta E_{CT}$  is small ( $-0.03$  eV). But because  $\Delta E_C (= -0.31$  eV/WB) is significant, the formation energy of the nearest-neighbor antisite pair is substantially reduced, to 5.1 eV per pair,<sup>6</sup> or 0.85 eV/WB. Table I summarizes the components of the wrong-bond formation energy

$\Delta E_{WB} = \Delta E_N + \Delta E_{CT} + \Delta E_C$ , showing that  $\Delta E_N$  and  $|\Delta E_C|$  increase as the band gap increases from that of GaAs to that of ZnSe, while  $|\Delta E_{CT}|$  decreases. The total wrong bond energy ( $\Delta E_{WB}$ ) increases with with the valence mismatch (2 in GaAs, 4 in ZnSe) between the two types of atoms.

Charge transfer and condensation will also exist in the randomized ZB compounds. We have directly calculated the enthalpy of randomization using the Special Quasirandom Structure (SQS) approach.<sup>8</sup> The SQS technique mimics the average structure of a random alloy by selecting the occupations of atomic sites in a supercell to best match the first few correlation functions of the infinite, perfectly random alloy. We have calculated the energy of diamond-like GaAs and ZnSe in the eight-atom SQS-4 supercell. Total energies were calculated using local density-functional theory, and first-principles pseudopotentials.<sup>9</sup> For ZnSe, the Zn 3d electrons were treated as valence states, using a mixed-basis approach.<sup>7</sup> For the GaAs special quasirandom structure, the atomic positions were relaxed using Hellman-Feynman forces. The relaxations were found to be negligible ( $\sim 0.01$  Å), with a relaxation energy of only 0.006 eV per atom, so size mismatch effects are small. Relaxations were not calculated for ZnSe. The calculated randomization energy of the ZB structure,  $\Delta E_R$ , is 0.36 eV/atom in GaAs and 0.80 eV/atom in ZnSe. Since the random structure has, on average, one right bond and one wrong bond per atom, the energy per wrong bond,  $\Delta E_{WB}$ , is also 0.36 eV in GaAs and 0.80 eV in ZnSe. We have also calculated

TABLE I. Wrong bond energies in GaAs and ZnSe. All energies are in eV per wrong bond.  $\Delta E_N$  gives the energy for a pair of neutral isolated antisites.  $\Delta E_{CT}$  gives the energy gain when the charge transfer between the isolated antisites is allowed.  $\Delta E_C$  gives the energy gain when the antisites are brought to nearest neighbor positions.  $\Delta E_{WB}$  is the net wrong bond (WB) energy for fully compensated wrong bonds ( $\Delta E_{WB} = \Delta E_N + \Delta E_{CT} + \Delta E_C$ ).  $\Delta E_R$  is the energy of the diamond-like phase relative to the zinc-blende phase.  $\Delta E_R = 0.29$  eV for InSb.

	GaAs	ZnSe
$\Delta E_N$ : Form neutral pair	+0.78	+1.19
$\Delta E_{CT}$ : Charge transfer	-0.21	-0.03
$\Delta E_C$ : Bring together	-0.27	-0.31
$\Delta E_{WB}$ : Total	+0.30	+0.85
$\Delta E_R$ (SQS): Randomization energy	+0.36	+0.80

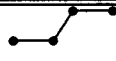


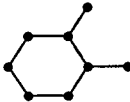
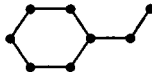
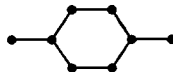
the energy of the random phase of InSb, and find that  $\Delta E_{WB} = 0.29$  eV. Note that these wrong bond energies are almost the same as those calculated for the nearest-neighbor antisite pair (Table I). Indeed, almost identical  $\Delta E_{WB}$  values were found in for Ga-Ga and As-As wrong bonds in calculations for GaAs/Ge superlattices ( $\Delta E_{WB} = 0.33$  eV)<sup>10</sup> and GaAs antiphase boundaries ( $\Delta E_{WB} = 0.35$  eV)<sup>11</sup>. This shows that charge compensation occurs in a variety of environments and is well characterized by  $\Delta E_{WB}$ .

The limits of the thermodynamic stability of the diamond-like random phase can be found from an Ising model for the diamond lattice, with coupling parameter  $J = \Delta E_R/2$ . The disordered phase would only be stable above the critical temperature  $T_c = 2.704J$ .<sup>12</sup> Our calculated values of  $\Delta E_R$  give  $T_c = 5,650$  K for GaAs and 12,550 K for ZnSe—well above the melting point of either compound. Despite this, *microscopic* regions of random order ("random aggregates", or RAs) in a GaAs crystal could occur. To investigate this, we picture a region of  $s \lesssim 10$  atomic sites, denoted  $RA_s$ , whose occupations are chosen randomly. Most RAs will change the stoichiometry of the crystal, and their formation energies will depend on the chemical potentials of the atoms of the crystal. For RAs that preserve stoichiometry, we can get a good estimate of RA

formation energies from  $\Delta E_{WB}$ , which, as noted above, is nearly constant in a variety of different environments. We approximate the formation energy of an RA by  $\Delta E_{WB}N_{WB}$ , where  $N_{WB}$  is the number of wrong bonds in the RA. This approximation will be valid for stoichiometric RAs that have wrong bonds near one another, maximizing compensation effects. Table II lists, for a range of  $s$ , geometric degeneracies and  $N_{WB}$  for a few low energy RAs that meet this condition. Also listed are approximate formation energies of these RAs in GaAs. RA formation energies are seen to be in the range of 3-6 eV, with concentrations of  $RA_4$  and  $RA_6$  of about  $1 \times 10^{12}$  and  $1 \times 10^9$  cm<sup>-3</sup> respectively, at  $T = 1500$  K (as estimated from a Boltzmann formula). For comparison, calculated energies of native point defects in Si,<sup>13</sup> GaAs,<sup>6</sup> and ZnSe<sup>7</sup> are in the range of 2-5 eV. Thus RAs containing *many* atoms can have formation energy comparable to point defects containing a *single* atom.

Under normal equilibrium conditions, the concentrations of RAs should be negligibly small. Significant concentrations of RAs could, however, exist in two cases. First, in GaAs with large deviations from stoichiometry, RAs with an excess of either Ga or As could be an efficient way of accommodating extra atoms. There are many more possible configurations of these non-stoichiometric RAs

TABLE II. Some low energy stoichiometric RAs. Each RA contains  $s$  atoms, with a geometric degeneracy  $D$ , and  $N_{WB}$  wrong bonds. Also shown are estimated RA formation energies,  $\Delta E_{RA} = E_{WB}N_{WB}$  in GaAs.

RA	$s$	$D$	$N_{WB}$	$\Delta E_{RA}$ (eV) in GaAs
	4	18	10	3.5
	6	2	12	4.2
	6	150	14	4.9
	8	48	16	5.6
	8	72	16	5.6
	8	24	16	5.6

than there are of stoichiometric ones. While stoichiometric RAs can be described as clusters of anti-site pairs, non-stoichiometric RAs cannot. Some of these RAs could have large equilibrium concentrations in either Ga-rich or As-rich material. Second, for material cooled rapidly from the liquid state, such as laser-annealed GaAs, large concentrations of RAs could be frozen in. Because of their low formation energy, RAs will anneal out slowly during cooling. A recent simulation of liquid GaAs using *ab initio* molecular dynamics techniques,<sup>14</sup> found that the liquid still contained many covalent bonds, of which 27% were wrong bonds between two Ga atoms or two As atoms. This high percentage of wrong bonds shows that the cost of a wrong covalent bond in random GaAs structures is very small, and gives further reason to believe that RAs are formed in fast-cooled samples. They also found that Ga-Ga wrong bonds occurred about twice as often as As-As wrong bonds in the liquid. This suggests that RAs may prefer being Ga-rich to being As-rich.

We now describe the expected structural and electronic properties of RAs. For a qualitative understanding of electronic properties of RAs, we first examine the density of states (Fig. 1) and selected charge density contours for the SQS of GaAs (Fig. 2). The As *s*-like state in the ordered ZB phase (A in Fig. 1a) gives rise to two states, P1 and P2 ( $-13$  to  $-9$  eV), that contain  $\sigma$ -like As-As bonds. The Ga,*s*-As,*p* bonds of ZB GaAs (B in Fig. 1a) are broadened to the P3 state of diamond-like GaAs ( $-9$  to  $-5$  eV), representing bonding

states with all three types of bonds. Next is P4 ( $-5$  to  $-4$  eV), a set of sharply peaked As-As bonding states, and P5 and P6 ( $-4$  to  $-2$  eV), two sets of Ga-As bonding states. The highest set of occupied states P7 and P8 ( $-2$  to  $0$  eV), consists of Ga-Ga bonding states mixed with As antibonding states. The band gap of the ZB phase is filled by two sets of unoccupied As antibonding states, P9 and P10 ( $0$  to  $2$  eV). Note that the heteropolar gap of or-

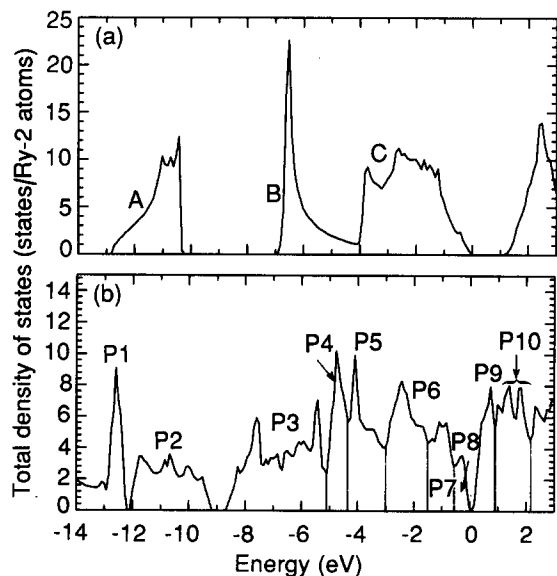


FIG. 1. Density of states for zinc-blende (a) and random (b) GaAs. The valence band maximum is the zero of energy.

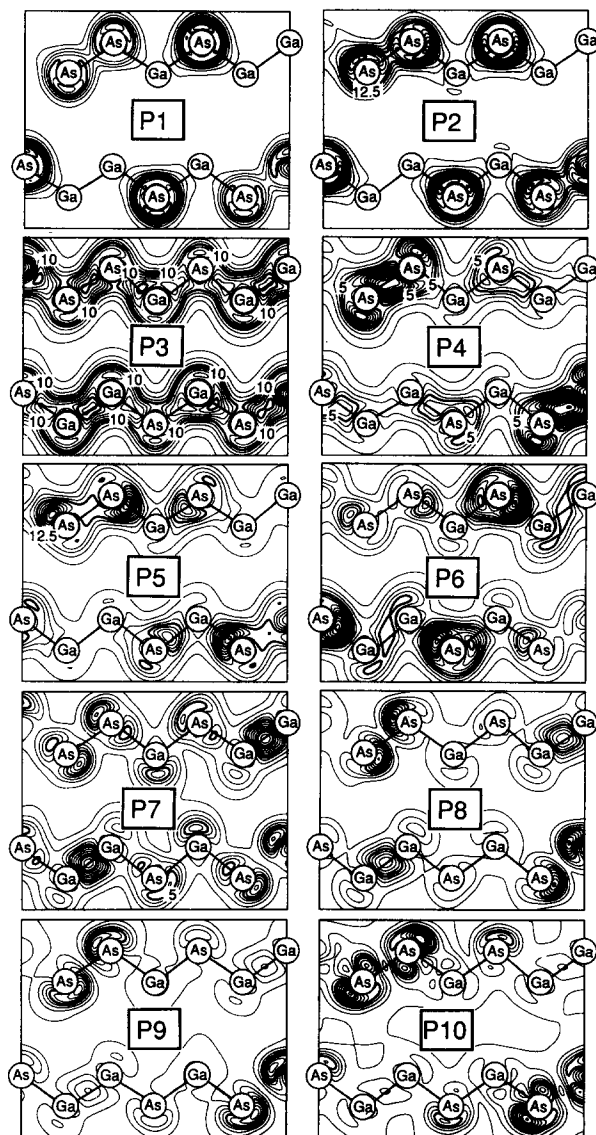


FIG. 2. Charge densities contours for states of the random GaAs structure. The labels refer to energy ranges shown in Fig. 1b. Shown in order of increasing energy are (P1 and P2) As *s* states, (P3) Ga-As, Ga-Ga, and As-As bonding, (P4) As-As bonding, (P5 and P6) Ga-As bonding, (P6) Ga-As bonding, (P7 and P8) Ga-Ga bonding with As antibonding, and (P9 and P10) As antibonding states.

dered GaAs is significantly reduced by the presence of the P2 states, and that the sharp peak at  $-6$  eV in the ordered structure is greatly broadened (P3). The band gap of SQS GaAs is reduced to nearly zero; SQS ZnSe actually becomes a metal.<sup>15</sup>

**Structural Properties.** Unlike point defects, which usually have only one (or a few) low energy configuration, RAs can have many low energy configurations. Because they come in such a large variety, RAs will exhibit a spread of properties. RAs can vary in three different ways: size, shape and chemical composition. (i) The size of an RA,  $s$ , can range from a minimum of 3 or 4 atoms up to a maximum in the range of 10 or 20. The formation energy and the degeneracy of the RA will increase with  $s$ . (ii) RAs can also exist in a variety of shapes; but compact shapes should be energetically preferred because they readily accommodate compensating charge transfer between wrong bonds. (iii) In an AB compound, some RAs have excess A (or B) atoms. These RAs may be an efficient way to accommodate deviations from stoichiometry in the crystal. (iv) Crystals containing dopants, or accidental impurities, can form new types of RAs by incorporating foreign atoms into their structure.

**Electronic Properties.** RAs can also exhibit unique electronic properties. (v) The electronic structure of diamond-like random GaAs contains states that cover most of the band gap of ordered GaAs (Fig. 1). Such states, which are predominantly As antibonding (P8, P9, and P10 of Fig. 2), will appear in RAs as electronic states in the band gap. These states will be extended over the volume of the RA ( $\sim 100\text{\AA}^3$ ) yet remain localized with respect to the rest of the crystal, just as electronic interface states are extended in the plane of the interface, but localized in the perpendicular direction. For GaAs with large RA concentrations, these states in the gap might be detectable spectroscopically. (vi) These states are potential recombination centers or carrier traps. Since these states will have a large extension compared to states associ-

ated with point defects, they should have small  $U$  values. Hence they may hold many electrons. (vii) RAs may have filled donor states or empty acceptor states in the band gap. Donor states in p-type material, and acceptor states in n-type, can lower their formation energy, and increase their concentration, by the exchange of electrons between the RA defect levels and the Fermi level (doping compensation). (viii) RAs can act as scattering centers, reducing the mobility of electrons and holes.

Although we have focused on RAs in ZB semiconductors, these defects may exist in any ordered compound. In compounds that easily form random alloys (such as GeSi, CuAu, or CuPt), RAs will have very low formation energies and may be involved in the phase transition from ordered to random structure. RAs may also exist in ionic compounds. In these materials, the RA formation energy would be governed by the size mismatch and charge transfer between A and B atoms.

In summary, we have calculated the energies of randomization for InSb, GaAs and ZnSe, and find them to be surprisingly small (0.29, 0.35, and 0.80 eV per atom, respectively). This reflects the compensating charge transfer between the two types of wrong bonds, and the electrostatic attraction of oppositely charged wrong bonds. Based on these results, we predict the existence of a new class of defects in ZB compounds, called random aggregates. Random aggregates of up to 10 atoms can have formation energies comparable to those of isolated point defects. These defects can have unusual structural and electronic properties, including electronic defect states that are extended over a few hundred  $\text{\AA}^3$ .

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